

# **Chemicals of Potential Concern (COPCs) Recommendations Fuel Additives**

## **Red Hill Bulk Fuel Storage Fuel Facility**

A meeting was held on May 10, 2016 to discuss the recommended approach to addressing the objectives of the Administrative Order on Consent (AOC) In the Matter of Red Hill Bulk Fuel Storage Facility (herein referred to as “the Facility”) Statement of Work (SOW) Section 6 and Section 7 with the Regulatory Agencies (State of Hawaii Department of Health [DOH] and United States Environmental Protection Agency Region IX [EPA]) and various subject matter experts (SMEs). The following attended the meeting: Parties of the AOC (Regulatory Agencies, Department of Navy [Navy], and Defense Logistics Agency [DLA]) and SMEs to the Regulatory Agencies (University of Hawaii [UH]; State of Hawaii Department of Land and Natural Resources [DLNR] Commission on Water Resources Management [COWRM]; United States Geological Survey [USGS] Pacific Islands Water Science Center; City and County of Honolulu Board of Water Supply [BWS]). Also in attendance were the Navy’s contractor, AECOM, and BWS’ contractor, Intera Geoscience & Engineering Solutions (Intera). One of the action items from the meeting was for the Navy and DLA to evaluate fuel additives and determine if additional analytes need to be included on the chemicals of potential concern (COPCs) list for the Facility, as previously agreed upon by the Parties of the AOC on February 4, 2016. The following discussion and table present the results of the fuel additives evaluation:

Table 1 summarizes 18 chemical constituents of additives associated with fuel stored at the Facility. Six groups of fuel additives were identified and evaluated: (1) metal deactivators; (2) corrosion inhibitors and lubricity improvers; (3) icing inhibitors; (4) static dissipaters; (5) lubricity improvers; and (6) antioxidants. To better assess and determine which chemical constituents could potentially pose a concern to the groundwater resource, the following attributes were evaluated for each additive group and associated chemical constituents: estimated/projected quantities of chemicals present per 10,000 barrels of fuel; physical, chemical, and toxicity properties; and associated EPA and DOH screening criteria (if available).

Based on the information gathered and data evaluated, Table 1 details the following results:

- Four of the 18 chemicals, while common, are proprietary (trade-secret) and permitted chemicals for which no information could be obtained at this time. These 4 chemicals are:
  1. lubricity improver additive Infernum R655;
  2. trade secret polymer containing sulphur (chemical component, 10-30% by weight, of the static dissipater additive STADIS 450) in F-24 and JP-8;
  3. trade secret polymer containing nitrogen (chemical component, 5-10% by weight, of the static dissipater additive STADIS 450) in F-24 and JP-8; and
  4. NJ Trade Secret Registry #00850201001-5000 P (chemical component, 70-80% by weight, of the corrosion inhibitor and lubricity improver DCI-4A) in JP-5.
- Five of the 18 chemicals are already included on the COPCs list for the Facility:
  1. benzene;

2. ethylbenzene;
  3. toluene;
  4. xylene; and
  5. naphthalene
- Seven of the 18 chemicals have no associated regulatory screening criteria, and are present at extremely dilute concentrations in fuel and/or have very low water-solubility. Therefore, these seven chemicals are not anticipated to pose concerns for the groundwater resource. These 7 chemicals are:
    1. solvent naphtha (petroleum; chemical component, 10-30% by weight, of the static dissipater additive STADIS 450);
    2. dinonylnaphthylsulphonic acid (chemical component, 10-30% by weight, of the static dissipater additive STADIS 450);
    3. propan-2-ol (chemical component, 1-5% by weight, of the static dissipater additive STADIS 450);
    4. N,N-disalicylidene-1,2-propanediamine (the metal deactivator additive);
    5. tertiary butylated phenol;
    6. o-terbutylphenol; and
    7. 2,4,6-tri-terbutylphenol (chemical components of the antioxidant additive AO-37).
  - The Navy and DLA recommend the remaining two of the 18 chemicals to be added to the COPCs list for the Facility and analyzed during the first two monitoring events. Given the short half-lives and very low concentrations of these two chemicals in fuel (e.g., additive to bulk fuel ratios), the Navy and DLA further recommend these two chemicals be removed from the COPCs list if groundwater sampling results show chemical concentrations are not detected above screening criteria, similar to the approach agreed upon for the lead scavengers. These two chemicals are:
    1. 2-[2-methoxyethoxy]-ethanol (screening criterion of 800 µg/L) and
    2. phenol (screening criterion of 5 µg/L)

The half-lives of 2-[2-methoxyethoxy]-ethanol in water is 15 days and phenol in soil is less than 5 days. It is estimated that, at most, 26.4 gallons of 2-(2-methoxyethoxy)-ethanol may have been released as part of the 27,000-gallon Tank 5 fuel release in January 2014. Phenol is not a chemical constituent in additives used for the fuel type released in January 2014. Furthermore, these two chemicals have the following properties:

- readily biodegradable and water-soluble;
- only present in fuel at small concentrations (i.e., at most, 2-[2-methoxyethoxy]-ethanol amounts to 410 to 615 gallons per 10,000 barrels of fuel and phenol amounts to 1.5% of 9.408 gallons of AO-37 additive per 10,000 barrels of fuel); and
- each chemical has associated EPA Tap Water Regional Screening Levels (RSLs)

EPA Method 8270D will need to be added to the sampling and analysis program proposed in the May 4, 2016 Work Plan/Scope of Work for AOC SOW Section 6 and Section 7 in order to analyze for these two chemicals.

Table 1. Summary of Chemical Information and Estimated/Projected Quantities of Fuel Additives, Red Hill Bulk Fuel Storage Facility, Joint Base Pearl Harbor-Hickam, Oahu, Hawaii

Additive	Addi- zation Site	Spe- cifica- tion	Description	Fuel	Approx. Max Additive Volume Added to Fuel	Chemical (Additive percent composition by weight)	CAS No.	Approx. Max Chemical Volume per Gallon of Fuel	EPA RSL (µg/L)	DOH EAL (µg/L)	Potential Receptors	Recommendation	Notes
Static Dissipater Additive (SDA) STADIS 450 Injected onsite	On-site Pearl Harbor	50 to 600 pS/m	If electrical conductivity additive is used, the conductivity shall not exceed 600 pS/m at the point of use of the fuel. When electrical conductivity additive is specified by the purchaser, the conductivity shall be 50 to 600 pS/m under the conditions at point of delivery.	F-24 and JP-8	1.331 gal per 10,000 barrels	Toluene (30-60%)	108-88-3	0.0000019 gal	1100	40	Human and ecological	Analyte is currently included on the COPCs list.	Investigation screening criteria is 40 µg/L.
						Solvent naphtha (petroleum), heavy aromatic (10-30%)	64742-94-5	0.00000095 gal	NA	NA	Ecological	Due to lack of regulatory screening criteria, negligible solubility in water, and very minimal volumes added to fuels (maximum 30% of 1.331 gallons added per 10,000 barrels), not recommended to add this analyte to the COPCs list.	Negligible solubility in water; moderate toxicity to aquatic organisms, and chronic aquatic toxicity is not expected due to low solubility in water and tendency to move from water to air. Biodegrades at a rapid rate and does not persist in the environment.
						Dinonylnaphthylsulphonic acid (10-30%)	25322-17-2	0.00000095 gal	NA	NA	Human and ecological	Due to lack of regulatory screening criteria, insolubility in water, and very minimal volumes added to fuels (maximum 30% of 1.331 gallons added per 10,000 barrels), not recommended to add this analyte to the COPCs list.	Insoluble in water. Very toxic to aquatic organisms.
						Trade secret polymer containing sulphur (10-30%)	NIF	0.00000095 gal	NIF	NIF	NIF	No information was found due to proprietary nature of analyte. Due to lack of information found and the very minimal volumes added to fuels (maximum 30% of 1.331 gallons added per 10,000 barrels), not recommended to add this analyte to the COPCs list.	NIF
						Trade secret polymer containing nitrogen (5-10%)	NIF	0.00000032 gal	NIF	NIF	NIF	No information was found due to proprietary nature of analyte. Due to lack of information found and the very minimal volumes added to fuels (maximum 10% of 1.331 gallons added per 10,000 barrels), not recommended to add this analyte to the COPCs list.	NIF
						Propan-2-ol (1-5%) (also known as isopropyl alcohol, isopropanol)	67-63-0	0.00000016 gal	410	NA	Human and ecological	This chemical has a short half-life in water and is present in extremely low concentrations in the fuels (maximum 5% of 1.331 gallons per 10,000 barrels),  Not recommended to add this analyte to the COPCs list at this time. However, if light non-aqueous phase liquid (LNAPL) is observed during groundwater sampling, it may be appropriate to re-evaluate this analyte.	Miscible in water, ethanol, ether, and chloroform. Estimated volatilization half-lives for a model river and model lake are 86 hours and 29 days, respectively. Biodegradation is expected to be an important fate process based on the results of microbial screening tests.
						Naphthalene (1-5%)	91-20-3	0.00000016 gal	0.17	17	Human and ecological	Analyte is currently included on the COPCs list.	Screening criteria is 17 µg/L.
Metal Deactivator (MDA) N,N- disalicy- lidene-1,2- propane diamine	Refinery	NA	MDA may be added to fuel to counteract the effects of metals known to be deleterious to thermal stability, such as copper, cadmium, iron, cobalt and zinc, provided that the nature of the contamination is reported. Where metallic contamination is unproven, an MDA may be used to recover thermal stability provided that the Thermal Stability Test (in accordance with Table 2) is determined before and after MDA addition and reported on the test certificate. Initial addition of more than 2.0 mg/L MDA is permitted when fuel will be transported in supply chains where copper contamination may occur; the maximum cumulative addition in Table 2 still applies. Note that fuel containing MDA has been shown to promote the dissolution of copper and may exacerbate thermal stability problems.	JP-5, F-24 and JP-8	0.9425 gal per 10,000 barrels	N,N-disalicylidene-1,2-propanediamine	94-91-7	0.0000022 gal	NA	NA	Human	Due to lack of screening criteria, low solubility, and very minimal volumes added to fuel (maximum 0.9425 gallons per 10,000 barrels), recommend not recommended to add this analyte to the COPCs list.	Mildly toxic by ingestion. When heated to decomposition it emits toxic fumes. In its pure form, the analyte is a solid at room temperature. Acute toxicity data (1960) indicates an LD50 of 4560 mg/kg via oral ingestion. Observed effects were depressed activity and weight loss or decreased weight gain.

Additive	Addition Site	Specification	Description	Fuel	Approx. Max Additive Volume Added to Fuel	Chemical (Additive percent composition by weight)	CAS No.	Approx. Max Chemical Volume per Gallon of Fuel	EPA RSL (µg/L)	DOH EAL (µg/L)	Potential Receptors	Recommendation	Notes
Infenium R655 (Lubricity Improver)	Refinery	520 micron max	Routinely used to improve the lubricity of military fuels and may be used in civil fuels. These additives vary in efficacy and may be depleted by adsorption on tank and pipe surfaces, so treat rates should be set with care. Because of their polar nature, these additives can have adverse effects on fuel filtration systems and on fuel water separation characteristics. For this reason, it is preferable to avoid adding more of these additives than needed.	F-76	145 ppm (equal to 60.9 gal per 10,000 barrels)	NIF	NIF	0.00015 gal	NIF	NIF	NIF	NIF	NIF
AO-37 (Antioxidant)- Only for Synthesized Paraffinic Diesel (AltAir)	Refinery	Contract and Refinery Based	Used to prevent the formation of oxidation deposits in engine fuel systems, to counteract the catalytic effects of active metals in fuel systems, and to improve the oxidation stability of fuels in storage.	F-76	22.4 ppm (equal to 9.408 gal per 10,000 barrels) currently (contract dependent)	Tertiary butylated phenol (>75%)	68610-06-0	0.000017 gal	NA	NA	NIF	Due to very minimal volumes added to fuels (9.408 gallons per 10,000 barrels) and lack of screening criteria, not recommended to add this analyte to the COPCs list.	Not found in Toxnet – toxicology data network. Physical properties of this chemical indicate a chemical density similar to water. Chemical structure is similar to o-terbutylphenol with the exception of more reactive –ene group instead of terbutyl.
						o-terbutylphenol (<10%)	88-18-6	0.0000022 gal	NA	NA	NIF	Due to very minimal volumes added to fuel (9.408 gallons per 10,000 barrels) and lack of screening criteria, not recommended to add this analyte to the COPCs list.	This substance is a colorless to yellow liquid which is soluble in alcohol, ether, isopentane, toluene and ethanol, and insoluble in water. Estimated chemical and physical properties for o-terbutylphenol indicate that this substance would adsorb to suspended solids and sediment in water, would slowly volatilize from water surfaces, and bioconcentrate in aquatic organisms. Limited empirical data, mainly derived by analogy to 4-t-butylphenol, indicate that 2-t-butylphenol may be resistant to biodegradation.
						2,4,6-tri-terbutylphenol (<15%)	732-26-3	0.0000034 gal	NA	NA	NIF	Due to very minimal volumes added to fuel (9.408 gallons per 10,000 barrels) and lack of screening criteria, not recommended to add this analyte to the COPCs list.	This substance is a liquid which is soluble in most organic solvents ethanol, acetone and carbon tetrachloride and is insoluble in water. Estimated chemical and physical properties for 2,4,6-tri-ter-butylphenol indicate that this substance would adsorb to suspended solids and sediment in water. Volatilization from water surfaces is expected but hindered by its preference to adsorb to suspended solids. Measured bioconcentration factors for this analyte in carp suggests bioconcentration is very high.
						Phenol (0.5-1.5%)	108-95-2	0.00000034 gal	5800	5	Human	Phenol has not been analyzed at thus far for the Facility, therefore, there is no data/information on the presence, absence, or concentration of phenol in the groundwater (if any). Since phenol is present in low concentrations in F-76 and LNAPL has not been observed thus far in at the groundwater table interface at the Facility, it is anticipated that phenol is not likely to be present in groundwater at levels suggesting a potential concern.  However, the Navy and DLA recommend analyzing for phenol during the first two groundwater monitoring events and based on those results, re-evaluating whether it should be retained on the COPCs list.	Phenol was not one of the many analytes in the historical data set for the Facility. The DOH Tier 1 EAL is based on gross contamination concerns (5 µg/L), which is lower than drinking water toxicity (11,000 µg/L, non-carcinogenic effects) and acute aquatic habitat impacts (3,400 µg/L). Phenol is a product of combustion of coal wood, municipal solid waste, and petroleum, and a product of auto exhaust. Although low levels of phenol have been detected in certain foods and tap water, these levels do not constitute major sources of exposure for most people. Phenol has been reported at concentrations of 7 and 28.6 ppm in smoked summer sausage and smoked pork belly, respectively. Phenol is readily biodegraded under both aerobic and anaerobic conditions in soil; half-life in soil is generally <5 days. Phenols generally do not adhere strongly to

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													soils and tend to be relatively mobile in water. Phenols are present in crude petroleum at low concentrations. Usually phenol concentrations are lower in refined petroleum, such as diesel fuel.
Fuel System Icing Inhibitor (FSII) (0.08%) Diethylene Glycol Monomethyl Ether	Refinery	0.08- 0.11%	Utilized to reduce icing effects of aviation turbine fuels. The quantity must be declared by the fuel supplier and agreed to by the purchaser.	JP-5	615 gal per 10,000 barrels	Ethanol, 2-(2- methoxyethoxy)-	111-77- 3	0.0015 gal	800	NA	Human	This analyte has a short half-life and is present in low concentrations in the fuel. There is an EPA tap water screening criterion and a known risk to human health.  The Navy and DLA recommend analyzing 2-(2-methoxy-ethoxy)-ethanol during the first two monitoring events and based on those results, re-evaluating whether it should be retained on the COPCs list.	High mobility in soils, not expected to volatilize from soil surfaces. Readily biodegradable (100%). Not expected to adsorb to suspended solids and sediments in water and volatilization from water is not expected. Half-life for water is 15 days. Biomedical effects: can be absorbed by skin and causes possible harm to unborn children.
				F-24 and JP-8	410 gal per 10,000 barrels			0.00098 gal					
Corrosion Inhibitor (CI) & Lubricity Improver (LI) DCI-4A	Refinery	NA	Routinely used to improve the lubricity of military fuels and may be used in civil fuels. These additives vary in efficacy and may be depleted by adsorption on tank and pipe surfaces, so treat rates should be set with care. Because of their polar nature, these additives can have adverse effects on fuel filtration systems and on fuel water separation characteristics. For this reason, it is preferable to avoid adding more of these additives than needed.	JP-5	1.331 gal per 10,000 barrels	NJ Trade Secret Registry # 00850201001-5000 P (70-80%)	NIF	0.0000025 gal	NIF	NIF	NIF	Due to proprietary nature of analyte, no information was found. Due to very minimal volumes added to fuels (maximum 80% of 1.331 gallons per 10,000 barrels), recommend to perform no further research on this analyte and not to include analyte on COPCs list.	NIF
						Xylene (20-30%)	1330- 20-7	0.00000095 gal 0.0000072 gal	190	20	Human and ecological	Analyte is currently included on the COPCs list.	Investigation screening criteria is 20 µg/L.
				F-24 and JP-8	10.06 gal per 10,000 barrels	Ethylbenzene (0-5%)	100-41- 4	0.0000012 gal	1.5	30	Human and ecological	Analyte is currently included on the COPCs list.	Investigation screening criteria is 30 µg/L.
						Benzene (0.02%)	71-43-2	0.0000000048 gal	0.46	5	Human and ecological	Analyte is currently included on the COPCs list.	Investigation screening criteria is 5 µg/L.

%	percent							LI	lubricity improver
µg/L	microgram per liter							m	meter
AO	antioxidant only							max	maximum
CAS	Chemical Abstracts Service							mg/kg	milligram per kilogram
CI	corrosion inhibitor							mg/L	milligram per liter
COPC	chemical of potential concern							MDA	metal deactivator
DOH	State of Hawaii Department of Health							NA	not applicable
EAL	environmental action level							NAPL	non-aqueous phase liquid
EPA	United States Environmental Protection Agency							NIF	no information found
F-24	NATO Fuel 24, jet fuel							NJ	New Jersey
F-76	NATO Fuel 76, marine diesel fuel							ppm	part per million
FSII	fuel system icing inhibitor							pS/m	picoSiemens per meter
gal	gallon							RHSF	Red Hill Bulk Fuel Storage Facility
JP-5	jet fuel propellant 5							RSL	regional screening level
JP-8	jet fuel propellant 8							SDA	static dissipater additive

Notes:

DOH EALs were based on Tier 1 Groundwater Action Levels for sites where groundwater is a current or potential drinking water resource, and the nearest surface water body is greater than 150 meters from site (DOH 2012).  
EPA RSLs were based on May 2016 Tapwater RSLs (EPA 2016).  
Shaded row indicates analytes recommended to be added on to COPCs list.

References:

Department of Health, Hawaii (DOH). 2012. Evaluation of Environmental Hazards at Sites with Contaminated Soil and Groundwater, Hawaii Edition. Office of Hazard Evaluation and Emergency Response. Fall 2011 (revised January 2012).  
Environmental Protection Agency, United States (EPA). 2016. Regional Screening Levels for Chemical Contaminants at Superfund Sites. EPA Office of Superfund. May.